The Effect of Dimercaptols of Acetonyl Acetone On the Polarographic Oxygen Overvoltage

By

JAMES CAREY BLALOCK

A DISSERTATION PRESENTED TO THE GRADUATE COUNCIL OF
THE UNIVERSITY OF FLORIDA
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA
September, 1950

TABLE OF CONTENTS

Page

LIST OF TABLES iii

LIST OF FIGURES. iv

Part

I INTRODUCTION 1

II EXPERIMENTAL 10

III DISCUSSION AND INTERPRETATION OF DATA. 19

IV SUMMARY. 49

BIBLIOGRAPHY. 50

ACKNOWLEDGMENTS 52

BIOGRAPHICAL NOTE 53

LIST OF TABLES

Table		Page
I	Comparison of Half-Wave Potential of First Oxygen Reduction Wave as Compared to the Dielectric Constant of the Solvent	20
II	Effect of Dimercaptols on the Half-Wave Potential of Oxygen in Methanol.	22
III	Shift of the Half-Wave Potential of Oxygen due to Presence of Dimercaptols in Methanol.	22
IV	Effect of Dimercaptols on the Half-Wave Potential of Oxygen in Ethanol	23
V	Shift of the Half-Wave Potential of Oxygen due to Presence of Dimercaptols in Ethanol.	23

LIST OF FIGURES

Figure		Page
1	Wiring Diagram of Sargent Model XII Polarograph	11
2	Construction Method of Evaluation of Half-Wave Potential.	16
3	Polarograms of First Oxygen Wave in the Presence of 1×10^{-3} M Dimercaptols in Methanol.	31
4	Polarograms of the First Oxygen Wave in the Presence of 1×10^{-3} M Dimercaptols in Ethanol.	32
	Graphic Presentation of Half-Wave Potentials of Increasing Concentrations in Methanol of:	
5	Methyl Dimercaptol	33
6	Ethyl Dimercaptol	33
7	Propyl Dimercaptol.	34
8	Butyl Dimercaptol	34
9	Amyl Dimercaptol.	35
10	Hexyl Dimercaptol	35
11	Heptyl Dimercaptol.	36
12	Octyl Dimercaptol	36
13	Nonyl Dimercaptol	37
14	Composite Graph, Figures 5-12	38

Figure Page

Graphic Presentation of Half-Wave Potentials of Increasing Concentrations in Ethanol of:

15 Methyl Dimercaptol. 39

16 Ethyl Dimercaptol 39

17 Propyl Dimercaptol. 40

18 Butyl Dimercaptol 40

19 Amyl Dimercaptol. 41

20 Hexyl Dimercaptol 41

21 Heptyl Dimercaptol. 42

22 Octyl Dimercaptol 42

23 Nonyl Dimercaptol 43

24 Decyl Dimercaptol 43

25 Undecyl Dimercaptol 44

26 Dodecyl Dimercaptol 44

27 Composite Graph, Figures 15-24. 45

28 Comparative Study of the Effect on the Electrocapillary Curve of the Addition of Hexyl Dimercaptol to the Supporting Electrolyte 46

29 Comparative Study of the Effect on the Electrocapillary Curve of the Addition of Octyl Dimercaptol to the Supporting Electrolyte 47

30 Electrocapillary Curve for Chloroform and Lithium Chloride-Methanol Solution. 48

Part I

INTRODUCTION

The polarographic method of analysis was developed some twenty-five years ago by Professor Jaroslav Heyrovsky. The method is based on current-voltage curves obtained when electro-reducible or electro-oxidizable substances are electrolyzed in a cell containing a dropping mercury electrode. From the characteristics of the current-voltage curve both the kind and concentration of the electro-reducible or electro-oxidizable substance may be determined.

The instrument called the polarograph was invented by Heyrovsky and Shikata[17] in 1925. This instrument automatically obtains and records photographically the current-voltage curve. The photographed curves are called polarograms.

In the field of inorganic analysis, the polarographic method has been applied to practically all common metallic ions and reducible anions. This method is particularly adapted to trace determinations. Consequently, the method is becoming very valuable in organic chemistry and especially in the related fields of biochemistry and biology.

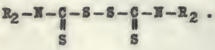
The past few years have seen a great advancement in the field of organic polarography. The most recent developments have involved reinterpretation of previous work, structure determination, reaction mechanism and kinetics, and quantitative estimation of compounds.

A large variety of organic compounds produce well-defined polarographic waves. Types of compounds which have been investigated at the dropping mercury electrode include aldehydes, ketones, unsaturated acids and hydrocarbons, heterocyclic compounds, organic halides, azo and diazo compounds.[21]

The disulfide linkage is apparently the only sulfur grouping which may be reduced at the dropping mercury electrode.[34] The reduction occurs not only when the disulfide group is attached to alkyl groups,

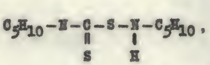
$$R-S-S-R,$$

but also when attached to the thiocarbonyl groups such as



$$R_2-N-\underset{\underset{S}{\|}}{C}-S-S-\underset{\underset{S}{\|}}{C}-N-R_2\ .$$

This reduction may be that of the dithiocarbamic acid, since Proske[25] reports the piperidine salt of pentamethyl dithiocarbamic acid,



$$C_5H_{10}-N-\underset{\underset{S}{\|}}{C}-S-\underset{\underset{H}{|}}{N}-C_5H_{10}\ ,$$

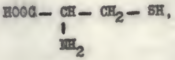
gives a reduction wave.

Allicin, $C_6H_{10}OS_2$, is reducible[8] and must be of the disulfide linkage, since Stone[31] reports that sulfoxides are not reducible.

Fraser and coworkers[10] found that the thiol grouping gives anodic waves and produces catalytic hydrogen waves if present on the alpha carbon of an acid or the beta carbon of an amino acid.

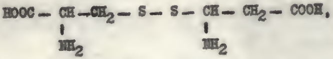
According to Gerber,[11] ethyl and normal butyl mercaptans give two anodic waves in ethanol solutions. The second wave is not reproducible.

Kolthoff and Barnum[19] have made extensive studies of the cysteine,



$$\underset{\displaystyle NH_2}{\mathrm{HOOC-\overset{}{CH}}}-CH_2-SH,$$

and cystine,



$$HOOC-\underset{\displaystyle NH_2}{CH}-CH_2-S-S-\underset{\displaystyle NH_2}{CH}-CH_2-COOH,$$

system. Cysteine can be oxidized to cystine by anodic electrolysis at a platinum electrode. The polarographic wave obtained by the anodic oxidation of cysteine did not correspond to the oxidation to cystine, but to the reversible reaction which does not occur at the platinum micro-electrode:

$$RSH + Hg \rightleftarrows HgRS + H^+ + e$$

The interpretation of the cathodic waves of cystine is quite involved. Kolthoff and Barnum obtained a pronounced maximum in a one-thousandth molar solution of cystine in tenth normal hydrochloric acid. The maximum was suppressed by the addition of capillary-active substances. The effect of these substances is very peculiar in that, in addition to suppressing the maximum, it shifts the polarographic wave to more negative potentials. The influence of varying concentrations of camphor is remarkable, as the wave is displaced to a more negative potential by almost one volt in a solution saturated with camphor.

To explain the shift of the cystine wave to more negative potentials, Kolthoff and Barnum postulated that the cystine has to be oriented or adsorbed into a favorable position at the surface of the mercury to be reduced. Apparently, capillary-active substances counteract or prevent the orientation or adsorption of the cystine at the interface and thus displace the wave to a more negative potential.

This interpretation is substantiated by the electrocapillary behavior of the camphor. The electrocapillary curves of tenth normal hydrochloric acid and the same medium saturated with camphor converge at approximately the same potential as the half-wave potential of cystine in the saturated camphor-hydrochloric acid mixture. At lower potentials, the mercury drop preferentially adsorbs the camphor. At the point of convergence of the electrocapillary curves the camphor is desorbed, and the capacity of the electrical double layer changes markedly.

Heyrovsky and Babicka[16] discovered a polarographic effect of proteins in an ammonium hydroxide-ammonium chloride buffer. The wave obtained was not due to the reduction of the protein but to the evolution of hydrogen catalyzed by the presence of the protein at the cathode interface. Analytical use has been made of this effect for the polarographic estimation of proteins. Bridka[3] continued the study of the protein effect and found that in ammoniacial solutions containing di- or tri- valent cobalt salts, sulfur-containing proteins produced double catalytic waves. The height of the waves increased with the concentration of the protein, but no linear relationship was found.

Bridka[2] also found cysteine and cystine to produce pronounced single catalytic waves in an ammonia buffer containing cobaltous or nickelous ions, but not in a buffer containing the trivalent ions. Bridka[4] attributes the catalytic cysteine wave to the fact that the cysteine forms a complex with divalent cobalt or nickel. In these complexes there is a co-ordination bond between the cobalt or nickel and the sulfhydryl group. This co-ordination bond weakens or activates the bond between the sulfur and the hydrogen of the sulfhydryl group, thus facilitating the deposition of hydrogen at the dropping electrode.

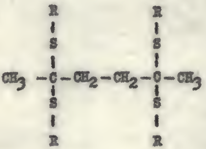
These catalytic waves are not specific for cysteine and cystine but may be applied to other compounds containing sulfhydryl or disulfide groups. For example, cysteyl glycine and thioglycollic acid give catalytic waves in the presence of divalent cobalt.[5]

After boiling in concentrated ammonia, mustard gas (β,β'-dichlorosulfide) may be detected polarographically by its catalytic wave in the presence of either cobaltous or cobaltic salts.[6]

Satori and Liberti[30] have investigated the cathodic and anodic behavior of mercaptobenzothiozol at the dropping mercury electrode. The cathodic waves were ascertained to be catalytic hydrogen waves. The anodic behavior did not correspond to the oxidation of a disulfide, but to the formation of a mercurous mercaptan. It may be recalled that the anodic behavior of cysteine did not correspond to the oxidation of cysteine to cystine.[19]

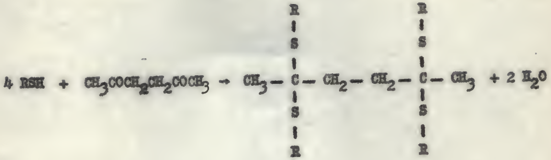
Danielli[9] and coworkers investigated various thiols in an attempt to confirm the structure of BAL-INTRAV (2-3 dimercaptopropanol glucoside) by the detection of a 1-2 dithiol grouping. Several representative thiols were examined polarographically in an ammonium hydroxide-ammonium chloride buffer containing cobaltous chloride. Alpha mercapto acids showed thiol peaks, whereas beta mercapto acids showed only a slight inflection at the same potential with no characteristic thiol peaks. Some indication of an inflection was obtained with thioethylene glycol. In the absence of a carboxyl group the polarographic detection of thiols is not possible.

The dimercaptols of acetonyl acetone, $CH_3COCH_2CH_2COCH_3$, are relatively new compounds of the general formula



$$CH_3-\overset{\displaystyle R\atop{|\atop{S\atop|}}}{\underset{\displaystyle {|\atop{S\atop{|\atop R}}}}{C}}-CH_2-CH_2-\overset{\displaystyle R\atop{|\atop{S\atop|}}}{\underset{\displaystyle {|\atop{S\atop{|\atop R}}}}{C}}-CH_3$$

where R— is usually a normal alkyl group. Posner[24] obtained the ethyl derivative. Rietz and coworkers[28,29] prepared the homologous series, methyl through normal dodecyl, in the University of Florida laboratories. The preparation of these compounds was by the interaction of the normal mercaptan with acetonyl acetone,



$$4\ RSH + CH_3COCH_2CH_2COCH_3 \rightarrow CH_3-\overset{\overset{\overset{\overset{R}{|}}{S}}{|}}{\underset{\underset{\underset{\underset{R}{}}{|}}{S}}{|}}{C}}-CH_2-CH_2-\overset{\overset{\overset{\overset{R}{|}}{S}}{|}}{\underset{\underset{\underset{\underset{R}{}}{|}}{S}}{|}}{C}}-CH_3 + 2\ H_2O$$

The original purpose of this research was the investigation of the reactions of these dimercaptols at the dropping mercury electrode. No reduction of these compounds was apparent at the dropping mercury cathode. However, when examined at the dropping cathode in the presence of oxygen, a remarkable shift of the first oxygen wave to more negative potentials was noted. This phenomenon is unusual since oxygen normally is easily reduced.

Heyrovsky[14] has shown that oxygen dissolved in solutions of electrolytes is easily reduced at the dropping electrode and produces two polarographic waves. Since oxygen is present at a concentration of approximately 2.5×10^{-4} molar in dilute aqueous solutions, its polarographic behavior is of tremendous practical importance. Heyrovsky[15] has further shown that oxygen may be determined quantitatively by polarographic methods in aqueous solutions. The first reduction wave, upon which the influence of hydrogen ion concentration is very small, in acid media is due to the reaction

$$O_2 + 2\ H^+ + 2\,e \rightarrow H_2O_2$$

or in alkaline media is due to

$$O_2 + 2\ H_2O + 2\,e \rightarrow H_2O_2 + 2\ OH^-.$$

The second wave corresponds to the reduction of hydrogen peroxide in acid solution,

$$H_2O_2 + 2\,H^+ + 2\,e \rightarrow 2\,H_2O,$$

or in alkaline solution,

$$H_2O_2 + 2e \rightarrow 2\,OH^-.$$

A well-pronounced maximum, easily suppressed by capillary-active substances, characterizes the first wave.[13,26,27,32]

Vitek[33] determined the ratio of the solubility of oxygen in ethanol, methanol and water. The ratio of solubilities is 20.5, 28.2 and 2.3, respectively. As a consequence, a greater diffusion current is obtained in the ethanol and the methanol media.

Kolthoff and Miller[22] have shown the potential at which the first oxygen wave starts to be practically independent of pH of the solution. This potential varies somewhat with the nature and concentrations of anions present. In dilute aqueous solutions of sulfuric acid, nitric or hydrochloric acid and in acetate buffers, the first wave starts at 0.15 volt when compared to the saturated calomel electrode. In dilute sodium hydroxide, the first wave starts at 0 volt. Kolthoff and Miller report the half-wave potential of the first oxygen wave to be practically constant at - 0.05 volt when compared to the saturated calomel electrode in ordinary buffer solutions between pH values 1 and 10 but is shifted to - 0.10 to - 0.15 volt in biphthalate buffers.

The reduction wave of hydrogen peroxide is quite flat with a reported half-wave potential of - 0.94 volt in buffer solutions from pH 2 to 10 in a supporting electrolyte of 0.1 N potassium chloride.[20]

Bridka and Tropp[7] have found the hydrogen peroxide wave to start at a more positive potential in the presence of traces of hemoglobin and hematin. Increasing concentrations of hemolyzed blood particles in an air-saturated sodium chloride solution cause the hydrogen peroxide wave to approach and finally to coincide with the first reduction wave of oxygen.

Generally, it is necessary to remove oxygen from a solution in practical polarographic work. This is usually accomplished by bubbling the solution to be electrolyzed with tank nitrogen or hydrogen. In neutral or alkaline solutions, oxygen may be removed by treatment with sodium bisulfite.

In view of the unusual effect of the dimercaptols upon the polarographic reduction of oxygen, the experimental work described in this dissertation is a study of the shift of the half-wave potential of the first reduction wave of oxygen caused by the presence of the dimercaptols.

Part II

EXPERIMENTAL

A Sargent-Heyrovsky Model XII photographically recording polarograph was used in this work. The wiring diagram for this instrument is shown in Figure 1. The instrument has a constant speed motor which drives the bridge and camera. This simultaneously rotates the camera to produce a voltage abscissa and a current ordinate and imposes an increasing fraction of the voltage applied across the bridge to the electrolytic cell, the rate of increase being proportional to the rotation of the camera.

All potential measurements were made with a Gray "Queen" potentiometer connected in parallel with the electrolytic cell. The potentiometer was standardized against a Weston Standard Cell for each potential measurement.

The mercury used as the dropping cathode and for the anode pool was purified by passage in a fine stream through columns containing dilute nitric acid, dilute sulfuric acid and water, respectively. A final purification was effected by distillation under a reduced pressure of approximately two millimeters.

The proper drop rate for most polarographic work is the most rapid which will give reproducible diffusion currents. If the drop time is too slow, difficulties in the construction method for evaluation of the half-wave potential are encountered. The evaluation of

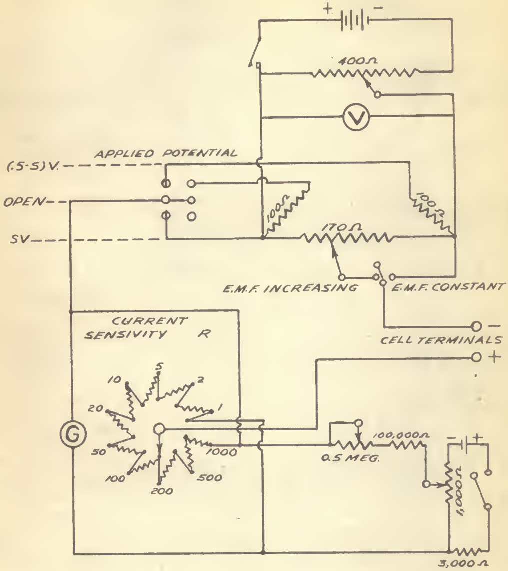


Figure 1.

Wiring diagram. Sargent Model XII Polarograph.

half-wave potential is discussed later. A drop time of 1.5 seconds per drop was used for recording the polarograms. A capillary of three inches in length with a bore of 0.05 millimeter was satisfactory.

A slower drop time was used in obtaining the data for the electrocapillary curves in order to obtain a larger difference in drop time at varying potentials. For this phase of the work a capillary three inches in length with a bore of 0.03 millimeter, having a drop time of 4.0 seconds per drop, was used. Final adjustment of the drop time was regulated by the height of the mercury resevoir.

The compounds studied were supplied through the courtesy of Dr. E. G. Rietz, of this Department, from another research project.[28,29] All compounds were obtained in the pure state with the exception of the normal propyl and normal hexyl dimercaptols. These were saturated with ethanol and purified by heating over a steam bath under reduced pressure, as suggested by Dr. Rietz.

Unfortunately, the dimercaptols are not sufficiently soluble in water for a study of their effect in aqueous medium. The lower homologues are sufficiently soluble in methanol and ethanol, and all members are extremely soluble in chloroform. The effect of these compounds on the half-wave potential of oxygen was studied in the solvents methanol and ethanol. Chloroform was used as the solvent for the higher homologues.

In the methanol series a 1 : 1 mixture of methanol-chloroform was employed for the heptyl dimercaptol, and chloroform alone was used for the octyl, nonyl, and decyl members. In the ethanol series the methyl through octyl homologues were sufficiently soluble in ethanol. An ethanol-chloroform mixture was used for the nonyl, and chloroform was used for preparing standard solutions of the decyl, undecyl and dodecyl members. The study of the undecyl and dodecyl compounds in ethanol and of the decyl dimercaptol in methanol were incomplete due to solubility limitations when added to the supporting electrolyte.

The addition of chloroform to the supporting electrolyte had no effect upon the half-wave potential of the first oxygen wave, although chloroform is reducible at the dropping mercury cathode at a reported half-wave potential of - 1.70 volts compared to the saturated calomel electrode.[20]

Absolute ethanol as supplied to the Department of Chemistry by Carbide and Carbon was found to be of sufficient purity. The methanol employed was Eimer and Amend Reagent Grade. The chloroform was from General Chemical, Reagent Grade. These solvents were used without further purification since they showed no impurities upon polarographic investigation.

Lithium chloride was chosen as the supporting electrolyte because of its solubility in the solvents employed and because of the electropositivity of the lithium ion. The lithium chloride was analytical grade and was dried overnight at 120°C. before use. All standard solutions were prepared in "Normax" volumetric flasks. "Normax" pipettes were used for all dilutions.

The type of electrolysis cell used for this work was of secondary importance.

All reported half-wave potentials are referred to the saturated calomel electrode. The method chosen for this reference is purely arbitrary since, at present, there is no known correlation of voltaic cells in aqueous and non-aqueous systems. However, this reference corresponds to polarographic data as reported in the literature. A saturated calomel cell was constructed in the usual manner and supplied with an agar bridge prepared from a suspension of agar and saturated potassium chloride to reduce junction potentials. It should be stated that the variations obtained with this cell proved to be well within the limit of error of ± 0.02 volt accepted for half-wave potentials.

A standardized procedure was used for the preparation of solutions for electrolysis. A 0.1 M solution of lithium chloride in the proper solvent was used as a supporting electrolyte. The concentrations of the dimercaptols were varied from approximately 2×10^{-5} M to 1×10^{-3} M. These were prepared from stock solutions of the dimercaptols in which concentrations ranged between 5×10^{-3} M and 1.3×10^{-2} M.

The typical procedure for obtaining a polarogram was: 0.05 milliliters of 1×10^{-2} M methyl dimercaptol in methanol was added to 10.0 milliliters of 0.1 M lithium chloride in methanol in the electrolysis cell with a resulting concentration of the methyl dimercaptol of 5×10^{-5} M. The solution was mixed well by stirring for approximately one minute. The dropping electrode was introduced, the intitial voltage read from the potentiometer, the polarogram recorded, and the final voltage was also read from the potentiometer. The dropping electrode was removed, and the saturated calomel electrode was introduced into the solution and the anode correction read from the potentiometer.

All polarograms which were taken of the first oxygen wave were rerun one or more times and were found to be entirely reproducible. The second wave was not reproducible for varying concentrations of the dimercaptols and therefore was not studied.

All polarograms were obtained at room temperature, approximately 30°C. For most practical polarographic work the temperature coefficient of the half-wave potential may be neglected.

A typical polarogram of the first oxygen wave in either solvent is shown in Figure 2. This figure will be used to illustrate the method of evaluating the half-wave potential by a construction method. A base, or reference line, ab, is drawn parallel to the base of the polarographic print. Perpendicular lines are dropped from $\underline{E}_1$ and $\underline{E}_2$, the initial and the final voltages as read from the potentiometer, to the base line ab. Tangents cd and ef are drawn to the residual and diffusion current lines, respectively. The perpendicular, gi, is raised from ab so that the distance gh is equal to hj. By construction in this manner, the distances x and y

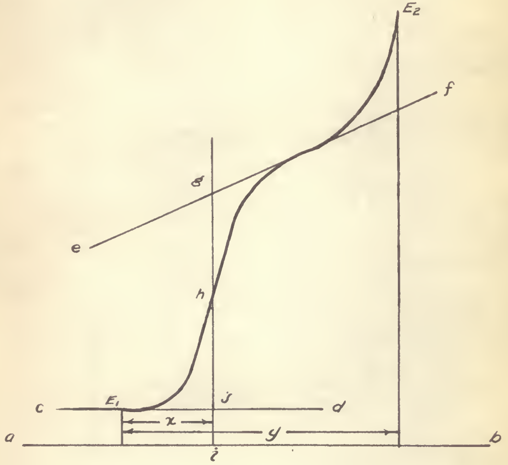


Figure 2.

Construction method of evaluating half wave potential.

may be related to the half-wave potential, $\underline{E}_{\frac{1}{2}}$, by the relation

$$\underline{E}_{\frac{1}{2}} = -\left[\frac{(\underline{E}_2 - \underline{E}_1)^x}{\underline{y}} + \underline{E}_1 - \underline{A}\right]$$

where $\underline{A}$ is the anode correction referring the half-wave potential to the saturated calomel electrode in reduction potentials.

A difficulty which is encountered in the construction method of estimating the half-wave in the presence of the higher homologues of the dimercaptols is evidenced in Figures 3 and 4. These figures are tracings of polarograms obtained of the first oxygen wave in the presence of 1×10^{-3} $\underline{M}$ solutions of the various dimercaptols in methanol and ethanol respectively. As illustrated by these polarograms, the first and second oxygen waves approach each other so closely as the size of the dimercaptol molecule increases that the above-described construction method for estimating the half-wave potential becomes doubtful.

To overcome this difficulty, it was decided to evaluate all half-wave potentials from the diffusion current of the first oxygen wave in the supporting electrolyte alone. The procedure developed was to determine the diffusion current, which corresponds to the distance $\underline{jg}$ in Figure 2 and which is due to the oxygen dissolved in the solution of supporting electrolyte for each series of determinations. Then the distance $\underline{hj}$, which is one-half the distance $\underline{jg}$ and is proportional to the diffusion current, is erected perpendicular to the base line ab from the line cd tangent to the reduction wave. It follows that the relationship given above may be used to calculate the half-wave potential from the distances x and y.

Half-wave potentials for various concentrations of solutions containing the dimercaptols were found to be constant within ± 0.02 volt.

Electrocapillary curves were determined for various solutions. The procedure was to measure the drop time at various applied potentials.

Part III

DISCUSSION AND INTERPRETATION OF DATA

The dimercaptols were subjected to cathodic electrolysis at the dropping mercury electrode. Careful examination in both methanol and ethanol solutions up to applied potentials of approximately - 2.4 volts showed no reduction wave in the absence of oxygen. As mentioned previously, the disulfide linkage is apparently the only sulfur grouping which may be reduced at the dropping mercury electrode.[34]

The half-wave potential of the first reduction wave of oxygen was found to be - 0.36 volt ± 0.01 volt in a 0.1 M solution of lithium chloride in methanol. In 0.1 M lithium chloride in ethanol, the corresponding half-wave potential was found to be - 0.43 volt ± 0.01 volt. These half-wave potentials are in reference to the saturated calomel electrode and were determined as described in the previous section. Addition of chloroform had no effect upon the half-wave potential in either medium.

These half-wave potentials differ from the value of - 0.05 volt reported by Kolthoff and Miller[22] for most aqueous solutions. These differences may be attributed to a change in overvoltage due to the change in solvent. It is interesting to note that the value of the half-wave potential becomes more negative as the dielectric constant of the solvent decreases. Table I is a comparison of the dielectric constant and half-wave potential for the different solvents.

TABLE I

Comparison of Half-Wave Potential of First Oxygen Reduction Wave as Compared to the Dielectric Constant of the Solvent

Solvent	Dielectric Constant[18]	Half-Wave Potential
Water	82.6	- 0.05 volt
Methanol	33.8	- 0.36 volt
Ethanol	26.5	- 0.43 volt

The data obtained for the various dimercaptols are best shown graphically. Figures 5 through 13 show the relation of the half-wave potential of the first oxygen wave to the concentration of the dimercaptol present in methanol solutions. The concentrations are expressed in millimoles per liter. Figures 15 through 26 show effects of varying concentrations of the dimercaptols upon the half-wave potential in ethanol solutions. As stated previously, solubility limitations prevented a study of the effect of decyl, undecyl and dodecyl mercaptols in methanol and of the undecyl and dodecyl compounds in ethanol.

Figures 14 and 27 are composite plots of the methanol and ethanol series respectively in the concentration range of approximately 0.1 to 1.0 millimoles dimercaptol per liter and show the effect of increasing the molecular size upon the half-wave potential. Concentrations of less than 0.1 millimole per liter are not shown in these figures since it is obvious that they will extrapolate to a common value.

Significant data from these graphs are shown in Tables II and IV. Table II gives the half-wave potential of the first oxygen wave for the various dimercaptols at concentrations of 1×10^{-4}, 5×10^{-4}, and 1×10^{-3} M in methanol. Table IV gives the oxygen half-wave potential at the same dimercaptol concentrations in ethanol.

Tables III and V illustrate the magnitude of the shift of the oxygen half-wave potential due to the presence of the above concentrations of dimercaptols.

It is evident that the concentration and the molecular size of the dimercaptols are the controlling factors of the shift in half-wave potential. From these results, it may be inferred that the presence of the dimercaptols has a pronounced effect upon the oxygen overvoltage. Oxygen is extremely electrophylic as evidenced by its standard reduction potential of 0.682 volt[23] for the oxygen-hydrogen peroxide couple. In view of this potential, the effect is even more remarkable.

Polarographic overvoltage may be defined as the difference between the standard electrode potential as compared to the saturated calomel electrode and the half-wave potential compared to the same reference for a specific reduction half-reaction.

TABLE II

Effect of Dimercaptols on the Half-Wave Potential of Oxygen in Methanol

Dimercaptol Present	Half-Wave Potential		
	1×10^{-4} M	5×10^{-4} M	1×10^{-3} M
Methyl	- 0.38	- 0.39	- 0.41
Ethyl	- 0.39	- 0.43	- 0.45
Propyl	- 0.43	- 0.49	- 0.53
Butyl	- 0.47	- 0.55	- 0.60
Amyl	- 0.56	- 0.64	- 0.67
Hexyl	- 0.61	- 0.69	- 0.74
Heptyl	- 0.68	- 0.75	- 0.79
Octyl	- 0.69	- 0.75	- 0.79
Nonyl	- 0.75	...	...

TABLE III

Shift of the Half-Wave Potential of Oxygen due to Presence of Dimercaptols in Methanol

Dimercaptol Present	Shift in Half-Wave Potential		
	1×10^{-4} M	5×10^{-4} M	1×10^{-3} M
Methyl	- 0.02	- 0.03	- 0.05
Ethyl	- 0.03	- 0.07	- 0.09
Propyl	- 0.07	- 0.13	- 0.17
Butyl	- 0.11	- 0.19	- 0.24
Amyl	- 0.20	- 0.28	- 0.31
Hexyl	- 0.25	- 0.33	- 0.38
Heptyl	- 0.32	- 0.39	- 0.43
Octyl	- 0.33	- 0.39	- 0.43
Nonyl	- 0.39	...	...

TABLE IV

Effect of Dimercaptols on the Half-Wave Potential of Oxygen in Ethanol

Dimercaptol Present	Half-Wave Potential		
	1×10^{-4} M	5×10^{-4} M	1×10^{-3} M
Methyl	-0.44	-0.46	-0.48
Ethyl	-0.44	-0.46	-0.47
Propyl	-0.44	-0.49	-0.55
Butyl	-0.47	-0.53	-0.57
Amyl	-0.49	-0.56	-0.58
Hexyl	-0.57	-0.64	-0.68
Heptyl	-0.62	-0.71	-0.75
Octyl	-0.66	-0.73	-0.74
Nonyl	-0.67	-0.74	-0.79
Decyl	-0.73	-0.77	-0.78
Undecyl	-0.73	...	...
Dodecyl	...	...	...

TABLE V

Shift of the Half-Wave Potential of Oxygen due to Presence of Dimercaptols in Ethanol

Dimercaptol Present	Shift in Half-Wave Potential		
	1×10^{-4} M	5×10^{-4} M	1×10^{-3} M
Methyl	-0.01	-0.03	-0.05
Ethyl	-0.01	-0.03	-0.04
Propyl	-0.01	-0.06	-0.12
Butyl	-0.04	-0.10	-0.14
Amyl	-0.06	-0.13	-0.15
Hexyl	-0.14	-0.21	-0.25
Heptyl	-0.19	-0.28	-0.32
Octyl	-0.23	-0.30	-0.31
Nonyl	-0.24	-0.31	-0.36
Decyl	-0.30	-0.34	-0.35
Undecyl	-0.30	...	...
Dodecyl	...	...	...

Applying the Nernst equation to the half-reaction, $O_2 + 2\,H^+ + 2e \rightarrow H_2O_2$, $E^o = 0.682$ volt, the following equation is obtained:

$$E = E^o - \frac{RT}{2F} \ln \frac{A_{H_2O_2}}{A^2_{H^+} A_{O_2}} \qquad (1)$$

Introducing the appropriate constants, converting from natural logarithms and assuming that concentrations may be substituted for activities,

$$E = 0.682 - \frac{0.059}{2} \log \frac{C_{H_2O_2}}{C^2_{H^+} C_{O_2}} . \qquad (2)$$

Applying this equation to the polarographic wave

$$E_{\frac{1}{2}} = 0.682 - \frac{0.059}{2} \log \frac{C_{H_2O_2}}{C^2_{H^+} C_{O_2}} + E_v \qquad (3)$$

where $E_{\frac{1}{2}}$ is the half-wave potential and E_v is the polarographic overvoltage, these potentials referring to the hydrogen electrode. Since most polarographic data are referred to the saturated calomel electrode, it is necessary to introduce this potential into equation (3). The standard reduction potential of the saturated calomel electrode is 0.246 volt,[23] in reference to the hydrogen electrode. The equation now becomes

$$E_{\frac{1}{2}} = 0.436 - \frac{0.059}{2} \log \frac{C_{H_2O_2}}{C^2_{H^+} C_{O_2}} + E_v . \qquad (4)$$

By the construction method for evaluation of the half-wave potential, the concentration of oxygen is equal to the concentration hydrogen peroxide formed at the electrode surface. Then,

$$E_{\frac{1}{2}} = 0.436 + 0.059 \log C_{H^+} + E_v. \qquad (5)$$

Kolthoff and Miller[22] have reported the half-wave potential of the first oxygen reduction wave to be constant at − 0.05 volt as referred to the saturated calomel electrode in the aqueous buffer region 1 to 10, an exception being in biphthalate buffers.

Introducing this value of the half-wave potential into equation (5) and solving for E_v,

$$E_v = -0.481 - 0.059 \log C_H \qquad (6)$$

or

$$E_v = -0.481 + 0.059 \text{ pH} \qquad (7)$$

for a pH of 1

$$E_v = -0.422 \text{ volt}$$

at pH 3

$$E_v = -0.304 \text{ volt}$$

and at pH 5

$$E_v = -0.186 \text{ volt.}$$

From these calculations, it is seen that the overvoltage of the oxygen-hydrogen peroxide couple is dependent upon the pH of the solution.

Standard electrode potentials are not available in non-aqueous media or it would be possible to perform similar calculations for the media used. It may be assumed that the polarographic behavior of oxygen in methanol and ethanol with respect to pH is of the same magnitude as in aqueous solutions.

Glasstone[12] lists oxygen "bubble" overvoltages at various electrodes for normal sulfuric acid and potassium hydroxide. The term "bubble" overvoltage is the minimum overvoltage required to release the oxygen gas by electrolysis of the solution. The values listed vary from 0.06 volt for the nickel electrode to 0.53 volt for gold. No value is given for the mercury electrode.

That the nature of the solvent has an effect upon overvoltage is indicated by the various values of the half-wave potential of the first oxygen wave in water, methanol and ethanol.

All previous treatments of overvoltage have been limited to the effect of the three factors discussed above: the nature of the electrode; the solvent; and, to a lesser extent, a solute which is not involved in the electrode process.

However, the tremendous effect of the dimercaptols on the overvoltage of the oxygen-hydrogen peroxide couple necessitates the postulation of another factor involving overvoltages.

A correlation of the electrocapillary behavior of the dimercaptols and their effect upon the reduction of oxygen is believed to offer an explanation of the phenomenon.

An electrocapillary curve relates the potential of mercury and the surface tension at a mercury electrode-solution interface. The surface tension or drop time is dependent upon the potential of the mercury and the presence of capillary-active substances in the solution. The surface tension of cathodically polarized mercury first increases and then decreases with an increasing negative potential so that a normal electrocapillary curve has a parabolic shape.

The total surface tension is due to two effects.[21] First, attractive van der Waal forces on the surface atoms or molecules tend to contract the surface area. Secondly, an electrical contribution to the surface energy due to repulsive coulombic forces between fixed surface charges tends to increase the surface area and counteract the van der Waal forces. The net interfacial tension is decreased as a result of this electrical force. The change in surface tension according to the electrocapillary curve in the absence of capillary-active substances is due entirely to the change in magnitude and sign of electrical forces with changing applied potential. When the applied potential is zero, the mercury has a positive charge which decreases the surface tension at the interface. This positive charge is decreased by cathodic polarization of the mercury, and the surface tension increases until a maximum is reached. At this point, the electrocapillary maximum or the isoelectric point, the mercury is uncharged. Increasing cathodic potential decreases the surface tension until the streaming potential is reached.

Most inorganic and organic anions and organic compounds are capillary-active. Such substances lower the interfacial tension as a result of adsorption upon the mercury surface. The presence of organic capillary-active compounds may have different effects upon the shape of the electrocapillary curve. The general shape of the curve may not be altered, the only effect being the lowering of the surface tension. Frequently the presence of capillary-active substances flattens the upper portion of the curve. If the adsorbed substance is a dipole it may be adsorbed with the negative side on the mercury, resulting in a shift of the electrocapillary maximum to a more negative potential. On the other hand, if the dipole is adsorbed with the positive side adjoining the mercury the curve is shifted to a more positive potential.

All electrocapillary curves of surface-active substances coincide with the normal curve at more or less negative potentials. This indicates that the capillary-active substances are desorbed at such potentials.

Electrocapillary curves of the supporting electrolytes and of the same solutions containing dimercaptols were obtained. The normal electrocapillary curve of 0.1 M lithium chloride in methanol is shown in conjunction with the curve of the same medium that is 1×10^{-3} M with respect to the hexyl dimercaptol in Figure 28. Figure 29 shows the electrocapillary curves of a 0.1 M solution of lithium chloride in ethanol and the octyl dimercaptol in the same medium. Figure 30 is the electrocapillary curve of 0.1 M lithium chloride in methanol with one milliliter of chloroform added to ten milliliters of the methanol solution. The graph shows that chloroform has some effect upon the normal curve in that the drop time is increased slightly. The hexyl and octyl dimercaptols were chosen for Figures 29 and 30 for the reason that they are the highest homologues which could be studied in each of the alcohols without the aid of chloroform.

As shown in Figures 28 and 29, the presence of the dimercaptols causes the electrocapillary curve to become very flat initially, indicating a constant interfacial tension between the mercury drop and the solution. The fact that the drop time begins to decrease at approximately - 0.8 volt is worthy of note since - 0.79 volt apparently is the limiting value of the oxygen half-wave potential under these conditions.

The electrocapillary curves of the solutions containing the dimercaptols converge at - 1.4 volt with the normal curve of the supporting electrolyte. At this point the dimercaptol is probably desorbed from the mercury drop.

It is not to be inferred that all capillary-active substances affect the polarographic reduction of oxygen. The first reduction wave of oxygen has a maximum in aqueous solutions which does not appear in either methanol or ethanol solutions. This maximum is easily suppressed by addition of capillary-active substances such as methyl red, gelatin, and alkaloids[13,26,27,32] which have no effect upon the half-wave potential. Therefore, the shift in overvoltage is not due to the molecular weight since the molecular weight of the normal dodecyl dimercaptol is small— 832.2 — as compared to the enormous molecular weight of gelatin and alkaloids. Furthermore, surface activity as normally encountered has little effect when one considers the fact that gelatin produces no change in the half-wave potential.

Many inorganic anions such as chloride, bromide, iodide, sulfide and thiocyanate are capillary-active. Cations of substituted ammonium salts have been successfully applied to the elimination of polarographic maxima with no noticeable effect upon the half-wave potential of the reducible substance.[1]

In view of the electrocapillary behavior of the dimercaptols, it may be said that their extraordinary surface activity is a peculiar property of these compounds. That the interfacial tension at the dropping electrode-solution interface is constant up to approximately the same potential as that observed for the limiting half-wave potential indicates these compounds to be strongly adsorbed upon the mercury surface. When the interfacial tension begins to decrease it seems probable that desorption of the drop begins and that at this point the oxygen molecule may diffuse to the electrode. This is tantamount to saying that the dimercaptol is occluded upon the mercury drop preventing diffusion of oxygen to the electrode over a certain potential range.

The maximum shift in overvoltage was found to be -0.43 volt. From the relationship

$$\Delta F = -nFE$$

the free energy required for the shift in half-wave potential may be calculated. For the maximum shift, the calculated additional free energy change is 19.8 kilocalories.

It must be concluded that there is an additional effect on overvoltage other than that caused by the nature of the electrode, the solvent and the solute. This is caused by a particular property of certain capillary-active substances.

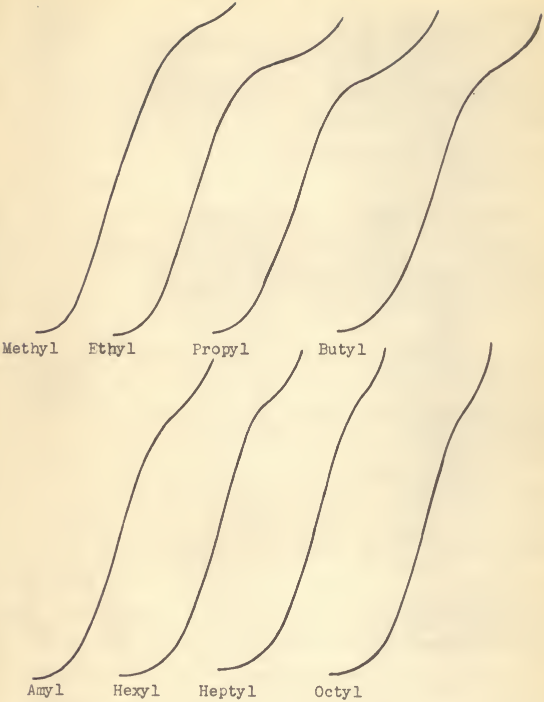


Figure 3.

Polarograms of the first oxygen wave in the presence of 10^{-3} M dimercaptols in methanol.

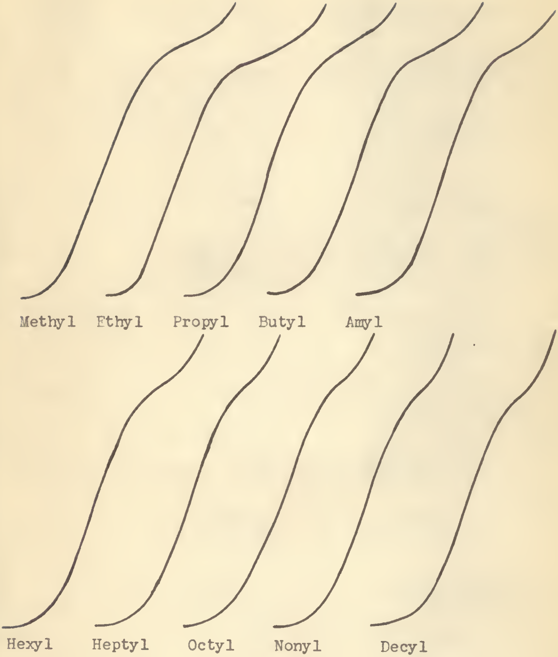


Figure 4.

Polarograms of the first oxygen wave in the presence of 10^{-3} M dimercaptols in ethanol.

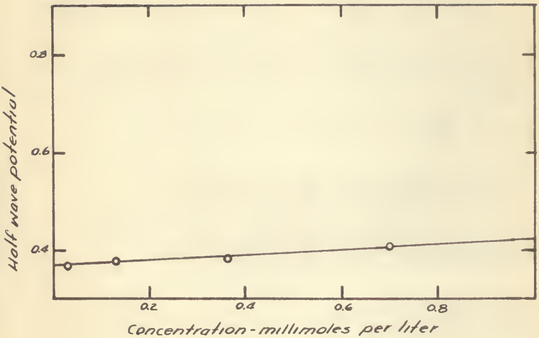


Figure 5. Methyl dimercaptol in MeOH.

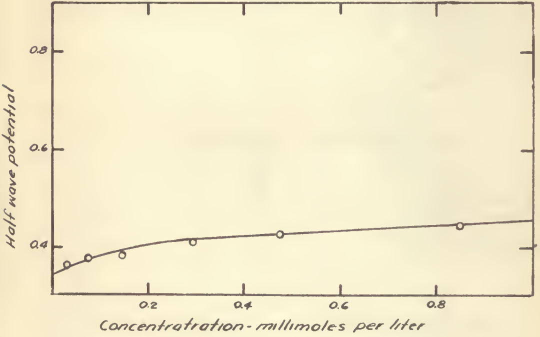


Figure 6. Fthyl dimercaptol in MeOH.

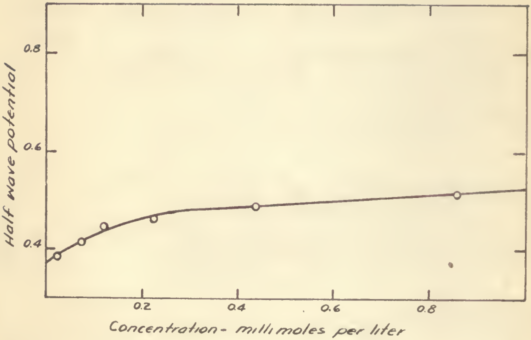


Figure 7. Propyl dimercaptol in MeOH.

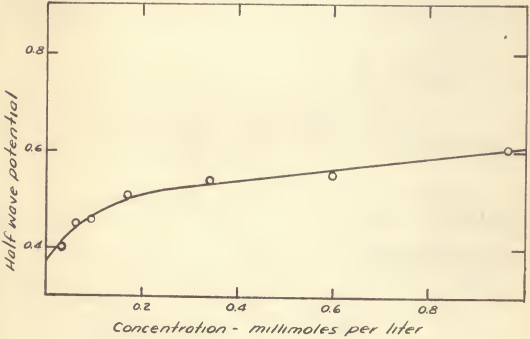


Figure 8. Butyl dimercaptol in MeOH.

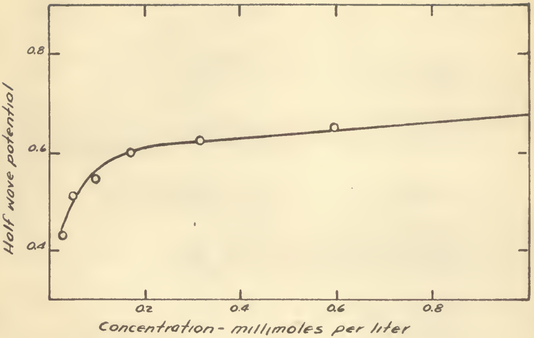


Figure 9. Amyl dimercaptol in MeOH.

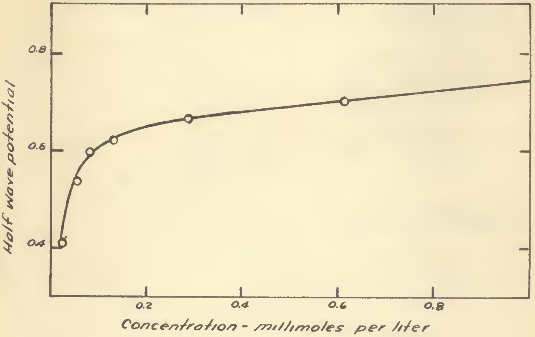


Figure 10. Hexyl dimercaptol in MeOH.

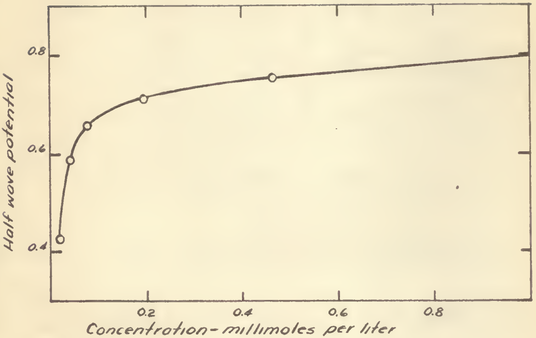


Figure 11. Heptyl dimercaptol in MeOH.

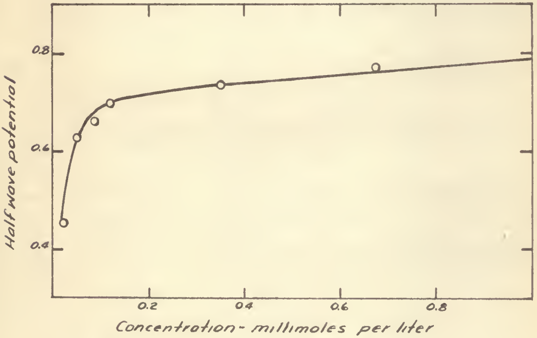


Figure 12. Octyl dimercaptol in MeOH.

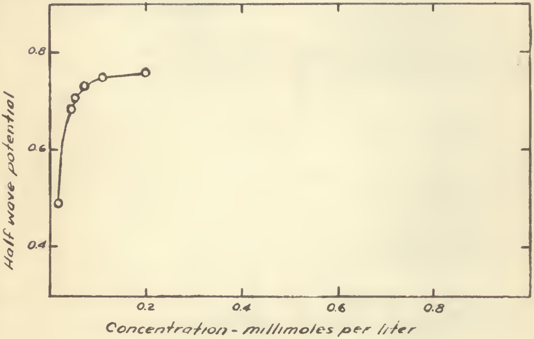


Figure 13. Nonyl dimercaptol in MeOH.

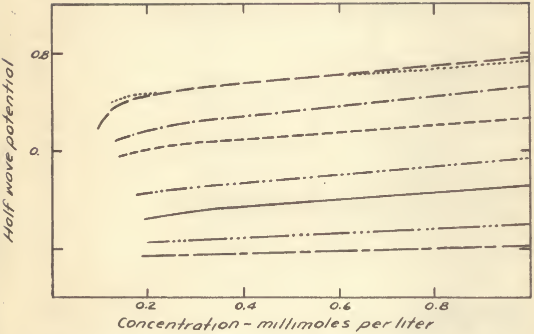


Figure 14. Dimercaptols in methanol.

Methyl
Ethyl
Propyl
Butyl
Amyl
Hexyl
Heptyl
Octyl

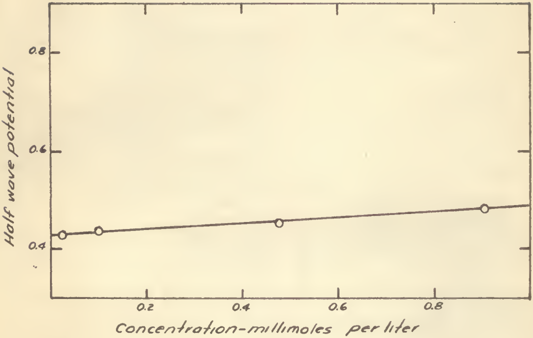


Figure 15. Methyl dimercaptol in ETOH

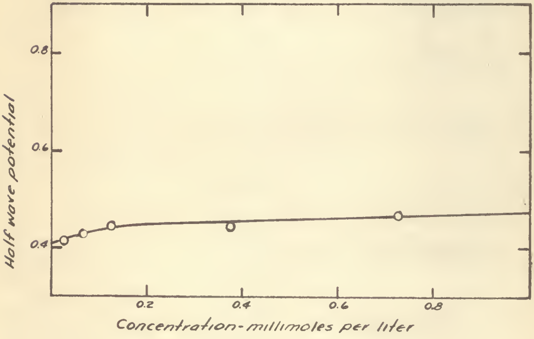


Figure 16. Ethyl dimercaptol in ETOH

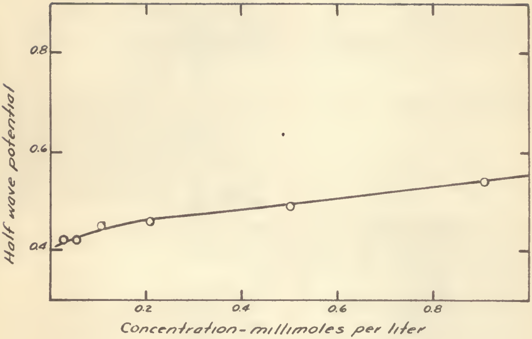


Figure 17. Propyl dimercaptol in ETOH

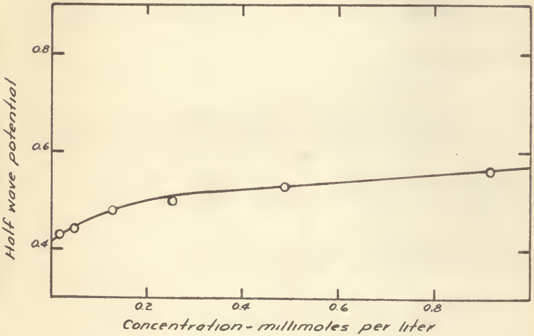


Figure 18. Butyl dimercaptol in ETOH

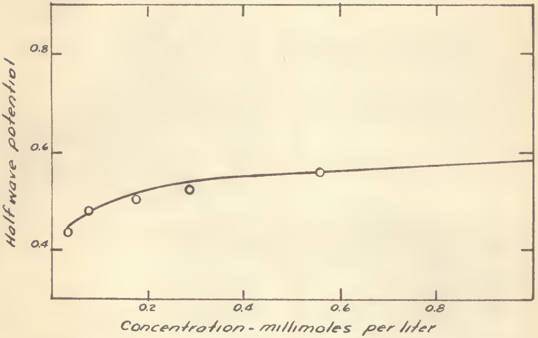


Figure 19. Amyl dimercaptol in ETOH

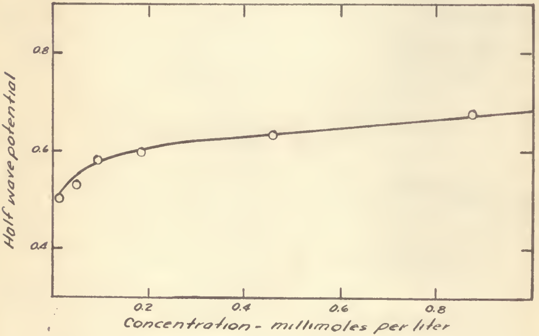


Figure 20. Hexyl dimercaptol in ETOH

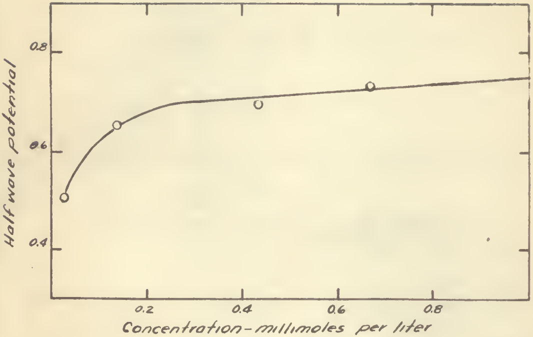


Figure 21. Heptyl dimercaptol in ETOH

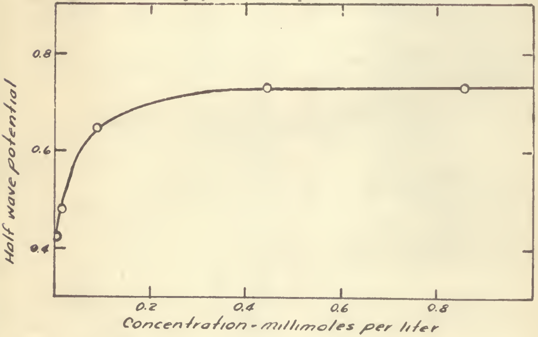


Figure 22. Octyl dimercaptol in ETOH

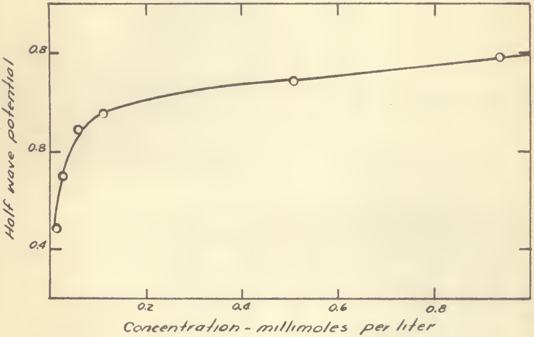


Figure 23. Nonyl dimercaptol in ETOH

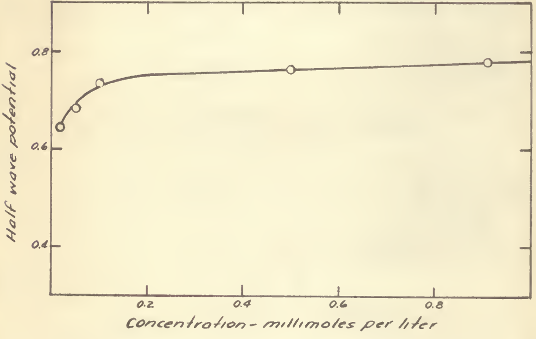


Figure 24. Decyl dimercaptol in ETOH

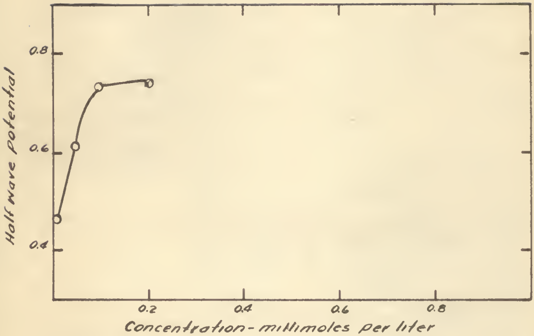


Figure 25. Undecyl dimercaptol in ETOH

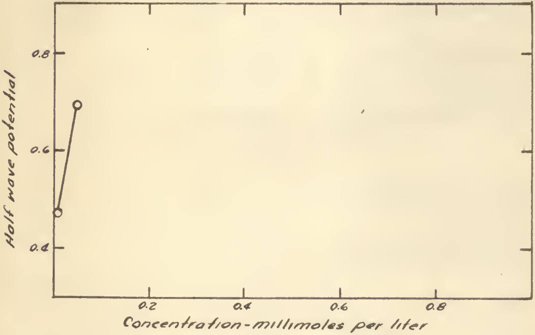


Figure 26. Dodecyl dimercaptol in ETOH

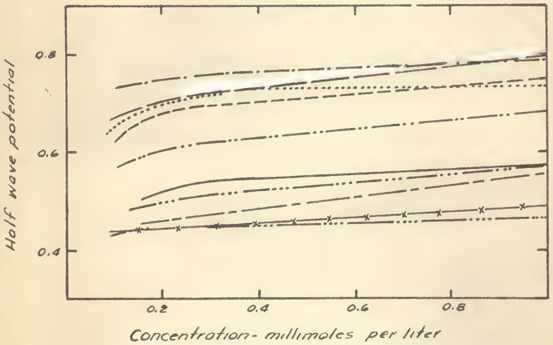


Figure 27. Dimercaptols in Ethanol.

——x——x——x—— Methyl ——··——··——·· Hexyl

——···——···—— Ethyl — — — — — — Heptyl

——–——–—— Propyl ················· Octyl

——···——···—— Butyl —— —— —— —— Nonyl

———————— Amyl ——·——·——· Decyl

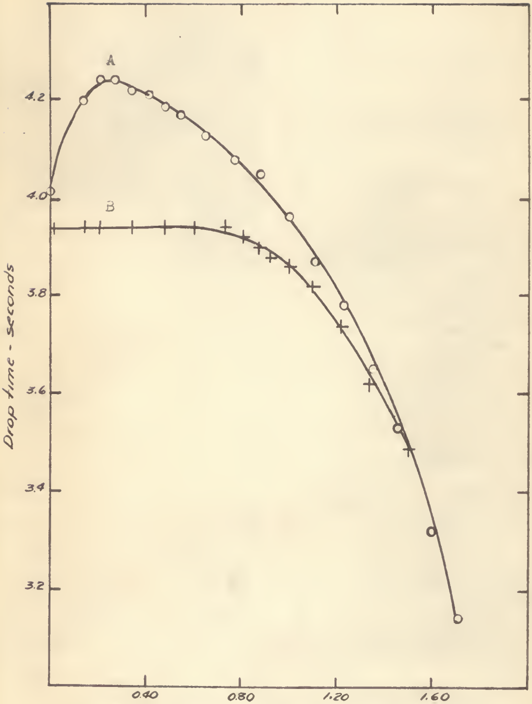


Figure 28. A. Electrocapillary curve, 0.1 M LiCl in MeOH.

B. Electrocapillary curve, $1x10^{-3}$ M Hexyl in 0.1 M LiCl.

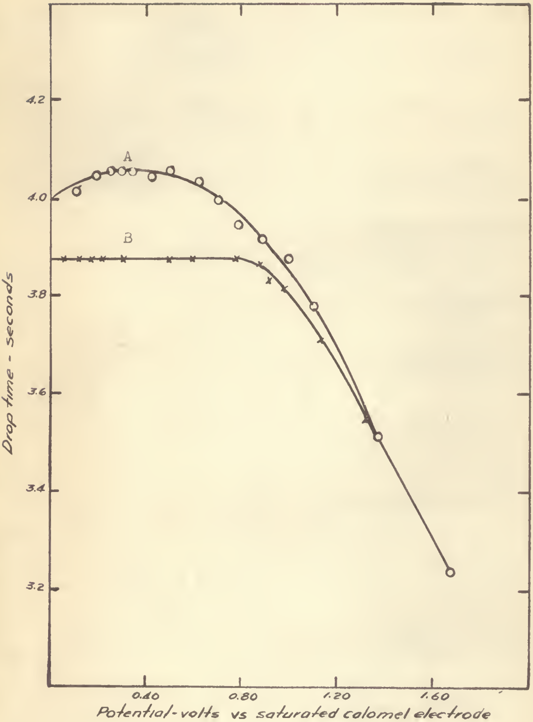


Figure 29. A. Flectrocapillary curve 0.1 M LiCl in FTOH.

B. Flectrocapillary curve $1x10^{-3}$ M Octyl in 0.1 M LiCl.

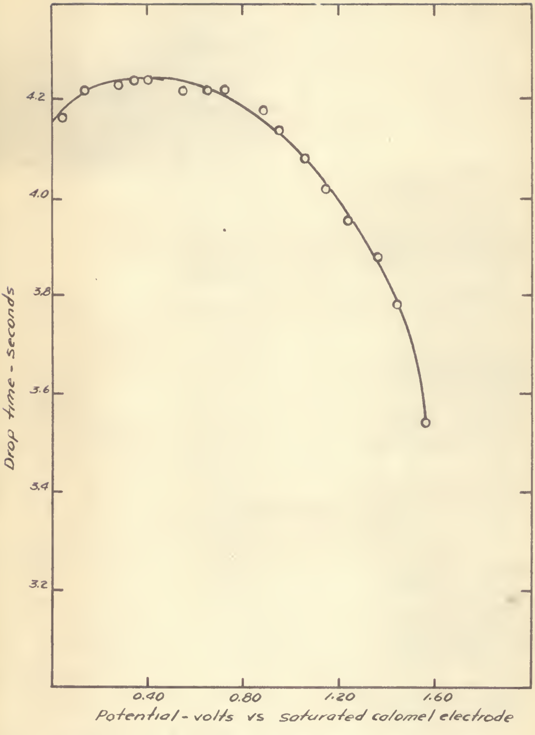


Figure 30. Flectrocapillary curve Chloroform in 0.1 M LiCl in MeOH.

Part IV

SUMMARY

The effect of the homologous series of the normal dimercaptols, methyl through dodecyl, of acetonyl acetone on polarographic oxygen overvoltages have been studied within solubility limitations in methanol and in ethanol solutions.

It has been found that both the concentration and the size of the dimercaptol molecule affect the half-wave potential of the first reduction wave of oxygen. The half-wave potential is shifted to more negative potentials to a limiting half-wave potential of - 0.79 volt.

This shift in half-wave potential is attributed to the electrocapillary behavior of the dimercaptols and is a contribution to the theories of overvoltage.

BIBLIOGRAPHY

1. Barrett, W. J., Unpublished Dissertation, University of Florida, 1950.

2. Bridka, R., *Collection Czechoslov. Chem. Commun.*, *4*, 148 (1933).

3. Bridka, R., *Collection Czechoslov. Chem. Commun.*, *5*, 112 (1933).

4. Bridka, R., *Collection Czechoslov. Chem. Commun.*, *5*, 148 (1933).

5. Bridka, R., *Biochem. Z.*, *272*, 104 (1934).

6. Bridka, R., *Collection Czechoslov. Chem. Commun.*, *9*, 76 (1937).

7. Bridka, R., and Tropp, C., *Biochem. Z.*, *289*, 301 (1936).

8. Cavillito, C. J.; Buck, J. S.; and Suter, C. M.; *J. Am. Chem. Soc.*, *66*, 1952 (1944).

9. Danielli, J. F.; Danielli, Mary; Fraser, J. B.; Mitchell, P. D.; Owen, L. N.; and Shaw, G.; *Biochem. J.*, *41*, 325 (1947).

10. Fraser, J. B.; Owen, L. N.; and Shaw, G.; *Biochem. J.*, *41*, 328 (1947).

11. Gerber, M. I., *Zhur. Anal. Khim.*, *2*, 1238 (1949).

12. Glasstone, S., "An Introduction to Electrochemistry." New York: D. Van Nostrand, 1942.

13. Hamamoto, E., *Collection Czechoslov. Chem. Commun.*, *5*, 427 (1933).

14. Heyrovsky, J., *Trans. Faraday Soc.*, *19*, 785 (1924).

15. Heyrovsky, J., *Casopis Ceskoslov. Lekarnictva*, *7*, 242 (1927).

16. Heyrovsky, J., and Babicka, J., *Collection Czechoslov. Chem. Commun.*, *2*, 270 (1930).

17. Heyrovsky, J., and Shikata, M., *Rec. trav. chim.*, *44*, 496 (1925).

18. "International Critical Tables. *6*" New York: McGraw-Hill, 1929.

19. Kolthoff, I. M., and Barnum, C., J. Am. Chem. Soc., 63, 3061 (1940).

20. Kolthoff, I. M.; Lee, T. S.; Crowell, W. K.; and Friess, S. L.; Anal. Chem., 22, 521 (1950).

21. Kolthoff, I. M., and Lingane, J. J., "Polarography." New York: Interscience Publishers, 1941.

22. Kolthoff, I. M., and Miller, C. C., J. Am. Chem. Soc., 63, 1013 (1941).

23. Latimer, W. M., "Oxidation Potentials." New York: Prentice-Hall, 1938.

24. Posner, T., Ber., 3, 2983 (1900).

25. Proske, G., Agnew. Chem., 53, 550 (1940).

26. Rasch, J., Collection Czechoslov. Chem. Commun., 1, 560 (1929).

27. Rayman, B., Collection Czechoslov. Chem. Commun., 3, 314 (1931).

28. Rietz, E. G.; Chapman, R. D.; and Fernandez, J. B.; J. Am. Chem. Soc., 70, 3486 (1948).

29. Rietz, E. G.; Fernandez, J. B.; Snider, L. T.; and Todsen, T. K.; J. Am. Chem. Soc., 71, 3433 (1949).

30. Satori, G., and Liberti, A., J. Electrochem. Soc., 97, 20 (1950).

31. Stone, K. G., J. Am. Chem. Soc., 69, 1832 (1937).

32. Varosova, Collection Czechoslov. Chem. Commun., 2, 8 (1930).

33. Vitek, V., Collection Czechoslov. Chem. Commun., 7, 537 (1935).

34. Wawzonek, S., Anal. Chem., 21, 61 (1949).

ACKNOWLEDGMENTS

The author is indeed happy to acknowledge the very valuable instruction, direction, assistance and inspiring guidance of Dr. Armin H. Gropp. Special appreciation is expressed to Dr. E. G. Rietz for information concerning the properties and the use of the compounds examined.

BIOGRAPHICAL NOTE

James Carey Blalock was born at Weldon, North Carolina, August 10, 1914. He was awarded the degree of Bachelor of Science in 1934 and the Master of Arts in 1937 by Wake Forest College. He served as Teaching Fellow in Chemistry at Wake Forest College from 1934 to 1937. In 1937 he was employed by the North Carolina Department of Revenue as a junior chemist. In 1941 he went to the Kankakee Ordnance Works, Joliet, Illinois, as production supervisor; and in 1943 he went to the Lion Chemical Corporation, El Dorado, Arkansas, as Assistant Chief Chemist. Mr. Blalock returned to Wake Forest College as Instructor in Chemistry in 1946; he came to the University of Florida as Interim Instructor in 1947.

COMMITTEE REPORT

This dissertation was prepared under the direction of the Co-Chairmen of the Candidate's Supervisory Committee and has been approved by all members of the Committee. It was submitted to the Graduate Council and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Date Sept. 2, 1950

T. M. Simpson
Dean

A. H. Gropp Jr
Co-Chairman

A. P. Black
Co-Chairman

J. E. Hawkins

R. C. Williams

H. E. Schweyer

Fred H. Heath

G. B. Butler